

# A Model for the Release of Adsorbed Molecules from the Surfaces of Airborne Particulate Matter Based on Liquid-Phase Desorption from Amorphous Carbon Blacks

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The release of molecules adsorbed on the surfaces of amorphous carbon blacks has been studied using liquid-solid chromatography. Adsorbate molecules, adsorbents, and mobile phases were selected on the basis of their relevance as models for the release of toxic agents adsorbed on inhalable environmental particulate matter that originates from the incomplete combustion of organic materials. The presence of surface active groups on the carbon blacks has been shown to adsorb and retain adsorbate molecules selectively, and this selectivity can be reduced by competition for these active groups by the displacing solvent. Release is also governed by the surface coverage of the particles and increases as coverage approaches the monolayer.

## Introduction

A previous paper (1) from this laboratory has reported on the adsorption of simple volatile organic molecules on well-defined amorphous carbon blacks using gas-solid chromatography and other standard methods. The rationale for this study was that simpler adsorbate-adsorbent systems, which contain many of the important physical and chemical parameters of the particulate complex, can be used to predict comparable adsorption data for environmental pollutants emitted during the incomplete combustion of organic materials. Although this study provided information on the types and amounts of molecules that could be expected to be found in the particulate complex, it could not provide information on the release (bioavailability) of the sorbed molecules after the particulate complex has been deposited in the lung. Such data are required in order to predict the potential health effects of inhaled particles of environmental origins.

The results presented in this paper attempt to complement the previous approach by including the release of the same molecules from the surfaces of the carbon

blacks into pure organic solvents, which have some of the solvent properties of the physiological fluids found in the alveolar region of the lung. The hypothesis of this research is that biologically active materials will only produce effects after they have been desorbed from the surface by physical or metabolic processes.

The determination of the concentrations of chemical agents sorbed upon airborne particles by solvent extraction with organic solvent is an important parameter; however, it assumes that all of these sorbed agents will reach the tissue and cause damage. In fact, the only way that the biological response can be related to the concentration of the chemical agent is to measure actual dose at the specific receptor responsible for the response. Such measurements are impossible to perform; therefore, this paper attempts to develop a method whereby the bioavailable dose can be predicted on the basis of physicochemical properties of the adsorbate-adsorbent complexes.

Many researchers have investigated the involvement of respirable particles in the release of adsorbed molecules; most have used benzo[a]pyrene as a model. Some of these studies have used modifications of normal lung physiological functions as end points to estimate release. Others have quantified chemically the release of benzo[a]pyrene. The major problem with most of these studies is that they have not quantified release as a function of the physicochemical properties of the particle-adsorbate complex, and therefore the results cannot be used

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for general prediction for the release of sorbed agents from the surfaces of particles of different environmental origins. Another potential drawback of the use of benzo[a]pyrene as a model is that this compound is non-polar and cannot be used as a model for polar adsorbed species. Therefore, it is important to study release as a function of the chemical properties of the adsorbed species.

Falk and Steiner (2,3) were the first group to investigate the desorption of benzo[a]pyrene and pyrene from the surfaces of carbon blacks. These researchers found that it was more difficult to extract these polynuclear aromatic hydrocarbons from the surfaces of the smaller-sized black (10–30 nm) (channel black) than the larger-sized black (30–160 nm) (furnace black). A subsequent study by Steiner showed that the adsorption of a carcinogen onto small particles of carbon black rendered it biologically inactive with respect to SC injection (4). Falk and co-workers (5,6), after showing that benzo[a]pyrene was not detectable in soot-laden human lungs, investigated the elution of polynuclear aromatic hydrocarbons adsorbed on soot particles by plasma proteins. These systems were found to extract different compounds to varying degrees.

Studies on the release of adsorbed molecules from the surfaces of carbon blacks were continued by Nau and co-workers (7,8), who tabulated the results of SC and IP injections of various carbon blacks in mice. They found that neither plasma nor gastric juices eluted significant amounts of adsorbed substances from the surfaces of furnace or channel blacks. They also determined that carcinogens could be deactivated (i.e., rendered biounavailable) by adsorption on a carbon black. Their inhalation studies with various animals revealed only the accumulation of the soot in the lungs without the production of malignant tumors. Pylev (9) found by intratracheal instillation that coarse blacks (304.7 nm) with low surface areas (10.6 m<sup>2</sup>/g) facilitated the elimination of benzo[a]pyrene as compared to smaller particles (12.8 nm, 250 m<sup>2</sup>/g). Contradictory results in terms of particle size were reported by Creasia and co-workers (10), who found that benzo[a]pyrene adsorbed on small particles (0.5 to 1.0  $\mu$ m) was eliminated more rapidly from the lungs of mice than benzo[a]pyrene adsorbed on larger carbon particles. These confounding results may be due to differences in the surface areas (surface coverage) and surface properties of the carbon particles, which were not reported in the latter study. Another explanation may be that there were different rates and modes of clearance for the different sized particles.

Carbon particles have been used to introduce other environmental agents into the lung. For example, Boren (11) demonstrated the ability of carbon particles to transport nitrogen dioxide into the lungs to produce destructive pulmonary lesions. This carrier mechanism could apply to other adsorbates depending upon the particle history and the interactions between the adsorbates and adsorbents. More recently, activated carbon particles have been used in combination with ali-

phatic aldehydes as models for cigarette smoke using as a biological end point the recruitment of polymorphonuclear leukocytes to airways (12). Increased responses were observed when the aldehydes were adsorbed on the respirable activated carbon. This increased response is probably due to either an increased focused dose at the tissue site, or possibly the aldehydes, were carried by particles to distal regions of the lung protected by the normal physiology of the upper respiratory tract. The activated carbon used in this study was not defined physically or chemically. Additionally, the use of aldehydes adsorbed on activated carbon may not be an optimum model for cigarette smoke since the latter is mainly composed of soluble tars rather than insoluble carbon particles, and therefore the clearance mechanisms will be very different.

There have been many studies that have reported the identities and extents of extraction of adsorbed molecules from the surfaces of different particles with various solvent systems. Some of these studies have attempted to relate modifications of normal physiological lung functions to the release of adsorbed molecules from specific particles, such as respirable particles found in urban air or in the emissions from mobile or stationary sources. However, these inhalation studies are difficult to interpret in terms of release of specific compounds since the physiochemical properties of these particulate complexes were not investigated and the compounds released were neither identified nor quantified. Attempts have been made to address this problem by the use of environmental samples doped with known concentrations of radiochemically labeled chemical carcinogens or mutagens (benzo[a]pyrene and 1-nitropyrene). It is our interpretation that these studies with carrier particles of environmental origins should be treated with considerable caution, because the doped molecules could be more biologically available than the same unlabeled molecules endogenous to the environmental particulate complexes. Most particles of environmental origin have supramonolayer coverages, and, therefore, doping these particles with radiolabeled adsorbates will not provide definitive information for the endogenous sorbed molecules which are retained by the surface more strongly since they will have been deposited at submonolayer coverages (1).

Bevan and co-workers have investigated the kinetics of the release of polynuclear aromatic hydrocarbons (particularly benzo[a]pyrene) from the surfaces of various carbon blacks into model phospholipid vesicles and rat lung homogenate using solution fluorescence spectrometry (13–16). Phospholipid vesicles composed of mainly dimyristoyl or dipalmitoyl phosphatidylcholines were used as models for the surfactant found in the alveolar region of the deep lung. These studies showed that the surface area (coverage) played a major role in release of adsorbed molecules since release increased with a decrease in surface area. Also, it was found that only a portion of the adsorbed molecules could be released, and it is reasonable to propose that the molecules released were less strongly bound. These studies quan-

tified release kinetically by incubating the PAH/carbon black complex with the physiological or model solvents at physiological temperatures but made no attempt to quantify adsorption or desorption on the basis of thermodynamics.

This current study attempts to address this deficiency and proposes liquid-solid chromatography as a method to model the release of adsorbed molecules from the particulate complex by the dynamic interaction with organic solvents that include some of the solvent properties of lung physiological fluids.

## Theory

The interactions between solute (*i*) and mobile phase (*m*) molecules and an adsorbent surface in liquid-solid chromatography can be expressed in terms of gas-surface (*a*) and solution (*s*) interactions (17,18):

$$i_m + (V_i/V_m)m_a \leftrightarrow i_a + (V_i/V_m)m_m \quad [1]$$

$$\Delta E_{isc} = - (V_i/V_m) \Delta E_m^a - \Delta E_{i,m}^s + \Delta E_{i,m}^a + \Delta E_i^a \quad [2]$$

where  $\Delta E_{isc}$  is the energy change for adsorption in the liquid phase measured by liquid-solid chromatography;  $\Delta E_i^a$ , and  $\Delta E_m^a$  are the energy changes measured for the gas-phase adsorption of solute and mobile-phase molecules;  $\Delta E_{i,m}^a$  is the interaction between adsorbed solute and mobile phase molecules;  $V_i$  and  $V_m$  are the molar volumes of the solute and mobile phase molecules, respectively; and  $\Delta E_{i,m}^s$  is the change in energy for the dissolution of solute molecules in the mobile phase. Experimentally, it has been proposed that the two center terms can be neglected since the energy changes that result from interactions between solute and mobile-phase molecules in the solution and adsorbed phases are small compared to the energy changes that accompany adsorption (18).

$$\Delta E_{isc} = - (V_i/V_m) \Delta E_m^a + \Delta E_i^a \quad [3]$$

While this approximation may be reasonable for polar adsorbents, such as silica or alumina, where the energies of interaction with the surface are strong compared to solute-solvent-surface or solution interactions, it has been questioned when nonpolar graphitized carbon blacks were used (19). In this latter study, the importance of the changes in the energy of solution was postulated. A previous gas chromatographic study from this laboratory (1) using amorphous carbon black has shown that if the solute is introduced in a solvent, then its heat of adsorption is less than the heat obtained by the introduction of pure solute. The explanation of these results is that the heat of adsorption on a heterogeneous surface decreases with increases in surface coverage by solvent and adsorbate molecules. Therefore, since there is a greater probability that the more abundant solvent molecules will be adsorbed on the most active sites, the solute molecules are more likely to interact with the less

active sites on the surface or pool with the adsorbed solvent molecules. As a result, the terms  $\Delta E_m^a$  and  $\Delta E_i^a$  will vary as a function of surface coverage ( $F\theta$ ). Since the adsorbent is always covered by a monolayer of solvent in liquid phase adsorption, the differential energy of adsorption for the mobile-phase molecules varies from high to lower energies. Therefore, when a solute molecule interacts with the surface, it can displace mobile phase molecule(s) that are held by either high or low energy sites on the surface.

$$\Delta E_{isc} = - (V_i/V_m) F\theta \Delta E_m^a - \Delta E_{i,m}^s + \Delta E_{i,m}^a + F\theta \Delta E_i^a \quad [4]$$

This interpretation will result in retention data being also dependent upon the concentration of the solute molecules which would be reminiscent of gas-solid chromatographic data. This conclusion is consistent with the research reported by Scott and Simpson (20), in which they measured retention data for a solute as a function of the addition of different concentrations of the solute (moderator) to the mobile phase. Their resulting data were used to obtain Langmuir solution adsorption isotherms.

For a homogeneous polar surface, there is less variation in energy sites as a function of coverage, and the energy of adsorption is constant. Similarly, if nonpolar graphitized carbon blacks are used as the adsorbents, the surfaces do not contain active sites due to increased order of the surface structure, and, therefore, interactions between the sorbed solute and mobile phase molecules become significant as compared to the interactions with the low energy sites on the graphite surface. The amorphous carbon blacks used in this study have heterogeneous surfaces with polar and nonpolar regions (1), so the polarity of the mobile phase and surface coverage will play major roles since under certain circumstances the active sites on the surfaces will dominate the separation, and at other times the interactions between the solute and mobile phase molecules will be important.

The significance of this discussion in terms of the prediction of the health risks associated with inhaled particulate complexes is that release of adsorbed molecules will be dependent upon coverage and the polarity of the biological fluid containing the desorbed species.

## Experimental

### Materials

The following mobile phases and adsorbates (99 + % purity, Aldrich or Burdick and Jackson) were used as received: 1-hexane, dichloromethane, tetrahydrofuran, methanol, water, benzene, thiophene, benzaldehyde, nitrobenzene, acetophenone, benzofuran, naphthalene, *p*-benzoquinone, hydroquinone, phenol, quinoline, pyridine, and aniline.

The ASTM classifications of the oil furnace carbon blacks adsorbents studied are as follows: N765, N339,

N110, N339 oxidized (N339 ox), and Black Pearls 2000 (BP 2000) (Cabot Corporation).

## Procedure

A liquid chromatograph with a variable wavelength UV detector  $\lambda_{254}$  (Varian 2000 Series) was used to investigate adsorption-desorption phenomena of all adsorbates. The carbon blacks used in this study are friable and cannot be packed using the balanced slurry packing technique. Therefore columns were packed with known weights of carbon blacks using vibration with vacuum assistance. Also, only short columns (5 cm, 6-mm OD, 2-mm ID) packed with the blacks (0.2 mm average particle size) and low flow rates (0.4 mL/min) were found to be stable for extended use. The mobile phases were degassed by sparging with helium.

Known aliquots (10  $\mu$ L) of solutions of the adsorbates in the mobile phase of interest (0.01%) were introduced via a liquid sampling valve (Rheodyne 7125) onto the chromatographic column, and separation temperatures were maintained using an oil bath. The columns were conditioned with each mobile phase prior to use. If a solute did not elute with the mobile phase under investigation, then the column was discarded and the entire experiment was repeated to ensure that the active sites remained available and were not blocked by retained solute molecules. Adsorption measurements were made isothermally at two column temperatures (22°C and 35°C). The void volume of the column was determined by injection without a column, followed by injection with the column empty. This retention volume minus the volume occupied by the known weight of carbon contained in the column, (based on the density of the carbon in the mobile phase), was used to calculate the void volume ( $V_m$ ). The liquid chromatographic retention data were recorded on a computing integrator (Spectra-physics SP4270).

Desorption isotherms were also obtained for selected adsorbates. A known amount of adsorbate was injected in the gas phase via a heated injection port onto a known weight of carbon contained in a column that was maintained at ambient temperature. This column was placed in the sample loop of a liquid sampling valve, and the desorption was monitored using a computing integrator which transmitted area slices as a function of time to a microcomputer (Apple IIe). The mobile phase was allowed to remove the air in the column packing before the column was connected to the detector. Software was developed to convert the area slice data to desorption isotherms.

Additionally, liquid adsorption isotherms were also determined from the shapes of elution chromatographic peaks using a modification of the approach suggested by Saint-Yrieix (21) for gas chromatographic data and software developed previously in this laboratory (1).

The dynamic chromatographic adsorption-desorption data were verified statically by incubating carbon with the same mobile phases containing known concentrations of an adsorbate (acetophenone) or by incubating

the carbons with preadsorbed adsorbate with the mobile phases. The adsorption or desorption of the adsorbate was monitored by gas liquid chromatography.

## Physical Characteristics of Carbon Blacks

The solvent densities of the blacks were determined by weighing the quantities of mobile phases required to fill a volumetric flask with and without known masses of carbon. Slight vacuum was used to remove air entrained in the pores of the carbon particles. These densities were used for the determination of column void volumes. The other physical properties of these blacks have been reported previously (1).

## Results and Discussion

Table 1 lists the solvent equivalent densities of the carbon blacks based on the mobile phases studied. These densities are less than their respective helium densities (1) and suggest that not all of the surface areas of the carbon particles are available to the mobile phases, probably as a result of the relative sizes of the pores and mobile phases. The distribution constant ( $K$ ) for each adsorbate, adsorbent, and mobile phase system were obtained using the following equations:

$$Ve = Vd + Vr \quad [5]$$

$$Vr = KW \quad [6]$$

where  $W$  is the mass of the carbon in the column,  $Vd$  is the void volume,  $Ve$  is experimental retention volume and  $Vr$  is the corrected retention volume. If solute distribution constants are obtained at two different temperatures ( $T_1$  and  $T_2$ ), then it is possible to obtain values for the change in enthalpy ( $\Delta H_{isc}$ ) for the various solutes:

$$-\Delta H_{isc} = (R T_1 T_2) (\ln K_2 - \ln K_1) / (T_2 - T_1) \quad [7]$$

where  $R$  is the gas constant. Tables 2–6 list the heats of adsorption that were obtained for the solutes as a function of the carbon black and the mobile phase. A positive heat indicates that the interactions between the solute and the surface dominate, whereas a negative heat indicates that the interactions between the solute and the mobile phase dominate. Systematic inspection of these data allows one to draw conclusions concerning the adsorbent surface properties and the thermodynamics of the adsorption of solute molecules from solution.

The carbon black N765 is less polar than the other blacks and has overall polarity comparable to 1-hexane. However, the surface of N765 appears to contain weakly acidic active groups (probably quinones,  $\pi$  acids) that interact more strongly with aniline as compared to the base quinoline. The importance of these weak active sites is decreased for solutes that do not contain functional groups with basic properties, and the solubility of the solute in the mobile phase or the interaction between adsorbed solute and mobile phase molecules dom-

Table 1. Densities of carbon blacks based on mobile phase.

Solvent	Carbon blacks, density, g/mL				
	N765	N339	N339 ox	N110	BP
1-Hexane	1.83	1.66	1.63	1.67	1.74
Dichloromethane	1.84	1.76	1.61	1.79	1.70
Tetrahydrofuran	1.76	1.70	1.58	1.66	1.70
Methanol	1.77	1.79	1.60	1.83	1.63
Water	1.81	1.74	1.61	1.59	1.64
Helium <sup>a</sup>	1.92	1.95	1.70	2.00	2.11

<sup>a</sup>From Risby and Sehnert (1).Table 2. Heat of adsorption<sup>a</sup> for the liquid-phase adsorption on carbon black N765.

Adsorbate	Mobile phase				
	C <sub>6</sub> H <sub>14</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O	CH <sub>4</sub> O	H <sub>2</sub> O
Benzene	- 13.4	- 0.6	- 16.0	8.3	NE <sup>b</sup>
Thiophene	- 13.6	0.6	- 17.9	4.1	- 19.0
Benzaldehyde	- 8.9	2.4	- 12.8	14.7	NE
Nitrobenzene	- 6.9	8.4	- 12.8	5.3	NE
Acetophenone	- 8.9	2.4	- 21.7	4.8	NE
Benzofuran	- 16.3	8.4	- 21.7	5.3	11.5
Naphthalene	- 7.5	13.4	- 17.9	11.3	NE
<i>p</i> -Benzoquinone	- 9.4	8.4	- 12.8	10.1	B <sup>c</sup>
Hydroquinone	NT <sup>d</sup>	NT	12.9	- 1.1	B
Phenol	- 13.6	28.5	- 16.0	8.3	B
Quinoline	- 13.8	10.3	- 10.2	23.6	NE
Pyridine	0.7	2.7	- 17.9	14.6	B
Aniline	0.9	13.4	- 10.4	8.3	B

<sup>a</sup>In kJ/mole.<sup>b</sup>NE, not eluted.<sup>c</sup>B, broad peak with no defined maximum.<sup>d</sup>NT, insoluble in mobile phase.Table 3. Heat of adsorption<sup>a</sup> for the liquid-phase adsorption on carbon black N339.

Adsorbate	Mobile phase				
	C <sub>6</sub> H <sub>14</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O	CH <sub>4</sub> O	H <sub>2</sub> O
Benzene	15.0	1.7	- 1.1	8.0	NE <sup>b</sup>
Thiophene	10.2	0.6	- 12.4	8.8	NE
Benzaldehyde	16.7	11.4	5.6	10.0	NE
Nitrobenzene	20.5	6.5	5.6	11.5	NE
Acetophenone	18.5	7.0	4.8	10.0	NE
Benzofuran	15.2	11.4	4.8	8.6	NE
Naphthalene	11.6	6.5	9.9	0.9	NE
<i>p</i> -Benzoquinone	22.6	11.4	9.4	6.2	NE
Hydroquinone	NT <sup>c</sup>	NT	17.3	- 1.5	NE
Phenol	NE	25.6	9.3	13.5	NE
Quinoline	NE	10.2	- 37.3	6.4	NE
Pyridine	B <sup>d</sup>	20.2	- 40.1	5.1	B
Aniline	NE	28.9	- 39.4	- 5.6	NE

<sup>a</sup>In kJ/mole.<sup>b</sup>NE, not eluted.<sup>c</sup>NT, insoluble in mobile phase.<sup>d</sup>B, with no defined maximum.

inates the values of  $\Delta H_{\text{isc}}$ . This conclusion is confirmed by the data obtained with the Lewis base mobile phase, tetrahydrofuran. This solvent competitively reduces the role of the weakly acidic active sites with the result that the interactions between the mobile phase and solute molecules dominate. N765 acts as a reverse-phase packing for the more polar solvents dichloromethane, methanol, and water.

Table 4. Heat of adsorption<sup>a</sup> for the liquid-phase adsorption on carbon black N339 oxidized.

Adsorbate	Mobile phase				
	C <sub>6</sub> H <sub>14</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O	CH <sub>4</sub> O	H <sub>2</sub> O
Benzene	34.8	2.6	18.8	58.8	NE <sup>b</sup>
Thiophene	22.8	- 8.4	10.5	35.7	NE
Benzaldehyde	B <sup>c</sup>	4.4	59.3	49.6	NE
Nitrobenzene	B	25.5	69.2	B	NE
Acetophenone	NE	- 8.2	62.8	B	NE
Benzofuran	8.0	20.8	61.3	B	NE
Naphthalene	b	54.3	50.0	B	NE
<i>p</i> -Benzoquinone	b	3.7	18.8	B	NE
Hydroquinone	NT <sup>d</sup>	NT	57.0	B	NE
Phenol	NE	10.2	9.9	37.4	NE
Quinoline	NE	NE	NE	NE	NE
Pyridine	NE	NE	NE	- 23.3	NE
Aniline	NE	NE	B	2.9	NE

<sup>a</sup>In kJ/mole.<sup>b</sup>NE, not eluted.<sup>c</sup>B, broad peak with no defined maximum.<sup>d</sup>NT, insoluble in mobile phase.Table 5. Heat of adsorption<sup>a</sup> for the liquid-phase adsorption on carbon black N110.

Adsorbate	Mobile phase				
	C <sub>6</sub> H <sub>14</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O	CH <sub>4</sub> O	H <sub>2</sub> O
Benzene	10.1	8.7	- 3.2	9.5	NE <sup>b</sup>
Thiophene	9.5	8.9	- 24.9	3.3	NE
Benzaldehyde	NE	- 0.3	- 0.6	NE	NE
Nitrobenzene	NE	5.9	15.2	B <sup>c</sup>	NE
Acetophenone	NE	0.4	- 3.0	B	NE
Benzofuran	NE	0.6	- 3.3	NE	NE
Naphthalene	NE	13.6	B	NE	NE
<i>p</i> -Benzoquinone	NE	- 10.2	B	NE	NE
Hydroquinone	NT <sup>d</sup>	NT	- 2.5	B	NE
Phenol	NE	- 1.2	- 9.8	3.8	NE
Quinoline	NE	- 28.1	NE	NE	NE
Pyridine	NE	- 37.4	- 3.3	14.1	NE
Aniline	NE	- 36.1	- 9.8	1.8	NE

<sup>a</sup>In kJ/mole.<sup>b</sup>NE, not eluted.<sup>c</sup>B, broad peak with no defined maximum.<sup>d</sup>NT, insoluble in mobile phase.

The other blacks, N339, N339 ox, N110, and Black Pearls, have more polar surfaces than N765 and contain greater numbers of acidic active groups (quinone-type) than are found in N765. The overall surface polarities of these blacks lie between dichloromethane and tetrahydrofuran. These blacks act as normal-phase column packings with less polar mobile phases and as reverse-phase packings with more polar solvents. There are a number of interesting conclusions which may be drawn from these data in terms of interactions between specific solutes and adsorbent surfaces. For example, hydroquinone interacts more strongly with the adsorbent surfaces than phenol, which suggests that the presence of two aromatic hydroxyl groups can be more important than the acid strength. Benzene interacts more strongly than thiophene, which suggests that there are graphitic structures on the carbon surfaces. Also, the introduction of functional groups onto benzene produces greater interactions with the surfaces of the carbons, but the

**Table 6.** Heat of adsorption<sup>a</sup> for the liquid-phase adsorption on carbon Black Pearls 2000.

Adsorbate	Mobile phase				
	C <sub>6</sub> H <sub>14</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O	CH <sub>3</sub> O	H <sub>2</sub> O
Benzene	NE	20.4	NE	NE	NE
Thiophene	9.6	8.4	NE	NE	NE
Benzaldehyde	NE	38.0	NE	NE	NE
Nitrobenzene	NE	41.3	NE	NE	NE
Acetophenone	NE	34.8	NE	NE	NE
Benzofuran	NE	22.9	NE	NE	NE
Naphthalene	NE	NE	NE	NE	NE
<i>p</i> -Benzoquinone	NE	40.9	13.0	NE	NE
Hydroquinone	NT	NT	NE	NE	NE
Phenol	NE	61.3	44.7	NE	NE
Quinoline	NE	NE	NE	NE	NE
Pyridine	NE	18.2	36.1	- 2.2	NE
Aniline	NE	33.4	NE	0.1	NE

<sup>a</sup>In kJ/mole.<sup>b</sup>NE, not eluted.<sup>c</sup>NT, insoluble in mobile phase.

interactions due to the functional groups are attenuated by the reduction in the interactions due to the aromatic  $\pi$  electrons with the graphitic  $\pi$  electrons. Pyridine interacts more strongly than benzene on all carbons with all the mobile phases except methanol, which shows that the interactions due to aromatic  $\pi$  electrons are less than acid-base interactions. If the data for naphthalene, quinoline, and benzofuran (two-ring systems) are compared, no trends can be discerned because the strengths of interaction are mobile-phase and carbon dependent; these results suggest that combinations of adsorption and solution interactions are responsible for retention and these combinations change with the polarities of the mobile phase. The partial oxidation of N339 (C<sub>346</sub>H<sub>21</sub>O<sub>10</sub>) to N339 ox (C<sub>208</sub>H<sub>13</sub>O<sub>10</sub>) produces a more active surface (1). The surface of the N339 ox clearly interacts with bases more selectively. The oxidation increases the number of  $\pi$  acid active sites.

Equation 4 may be expressed in terms of changes in enthalpy, and may therefore be used to examine the HPLC data contained in Tables 2–6 using the previously reported adsorption data obtained by gas-solid chromatography (1).

$$\Delta H_{isc} = - (V_i/V_m) F\theta \Delta H_m^a - \Delta H_{i,m}^s \quad [8]$$

$$+ \Delta H_{i,m}^a + F\theta \Delta H_i^a$$

Assuming that solute molecules interact directly with the carbon surface, evidenced by the variations in the heats of adsorption as a function of the carbon black, then the solute molecule must be displacing the mobile phase molecule(s) from the surface of the carbon black since, if the solute molecules were interacting with adsorbed mobile phase, the heat of adsorption would be independent of carbon black. In the liquid phase it has been proposed that multilayer adsorption does not occur (22), therefore, the term  $F\theta \Delta H_m^a$ , the heat of adsorption for the mobile phase molecules (at monolayer coverage) displaced by the solute molecules, can be approximated by 2/3 the heat of adsorption at low coverage (23). The term,  $\Delta H_{i,m}^a$ , is the heat of interaction between mobile

phase and solute molecules adsorbed on the surface of carbon, which may be obtained from the difference between the heat of adsorption of the solute, introduced as a solution in the mobile phase, and the heat of adsorption of pure solute. Therefore, it is possible to obtain values for the heat of interaction between the solute molecules and the mobile phase molecules in solution by the application of Equation 8. Examples of the results of these calculations, using the values for the molar volumes contained in Table 7, are listed in Table 8. The numerical values of these heats of solution are higher than expected, probably as a result of the errors associated with the approximation for the heat of adsorption of the mobile phase at monolayer coverage. An alternate explanation may be that the mobile phase molecules are displaced from sites on the surface with dif-

**Table 7.** Molar volumes of mobile phases and solutes.

	Molar volume
Mobile phase	
1-Hexane	131
Dichloromethane	64
Tetrahydrofuran	82
Methanol	41
Water	18
Adsorbate	
Benzene	89
Thiophene	79
Benzaldehyde	102
Nitrobenzene	103
Acetophenone	117
Benzofuran	108
Naphthalene	125
<i>p</i> -Benzoquinone	82
Hydroquinone	83
Phenol	92
Quinoline	118
Pyridine	81
Aniline	91

**Table 8.** Examples of calculations based on HPLC and GSC data.**A. Benzaldehyde on N765 as a function of mobile phase.**

Mobile phase	$(V_i/V_m)F\theta \Delta H_m^a$	$\Delta H_{i,m}^a$	$F\theta \Delta H_i^a$	$\Delta H_{isc}^a$
1-Hexane	35	5	86	47
Dichloromethane	62	- 3	86	24
Tetrahydrofuran	62	- 8	86	3
Methanol	118	3	86	- 2
Water	150	- 1	86	65 <sup>a</sup>

<sup>a</sup>Benzaldehyde not eluted; value is the sum of  $\Delta H_{i,m}^a$  and  $\Delta H_{isc}$ .**B. Various solutes on N765 with dichloromethane as mobile phase.**

Solute	$(V_i/V_m)F\theta \Delta H_m^a$	$\Delta H_{i,m}^a$	$F\theta \Delta H_i^a$	$\Delta H_{isc}^a$
Benzene	54	4	54	3
Acetophenone	71	21	101	53
Benzaldehyde	62	- 3	86	24
Nitrobenzene	62	6	88	40
Benzofuran	65	34	106	83
Quinoline	71	45	128	112

ferent energies and the energy released when the solute molecules adsorb by displacement will be solute and mobile phase dependent. However, the trend of the data is consistent with the solubility of the solutes in various mobile phases. If these results are considered in terms of expressing the general release of adsorbed molecules on the surfaces of airborne particles, then it is clear that the heat of interaction (solution) of the solute in the physiological fluid that is interacting with the surface of the particle (Fig. 1), the heat of adsorption of the solute on the surface (Fig. 2), and the coverage of the surface (Fig. 3) are major determinants of release.

Clearly, all the blacks irreversibly adsorb most of the solutes (except basic solutes with N765) when the mobile phase is water, and these results may be of environmental significance because they suggest that carbon particles could collect additional adsorbates in physiological fluids, which are composed of mainly water. This observation could have been predicted from the gas-solid chromatographic data, which showed that water interacted weakly with these carbon surfaces and there-

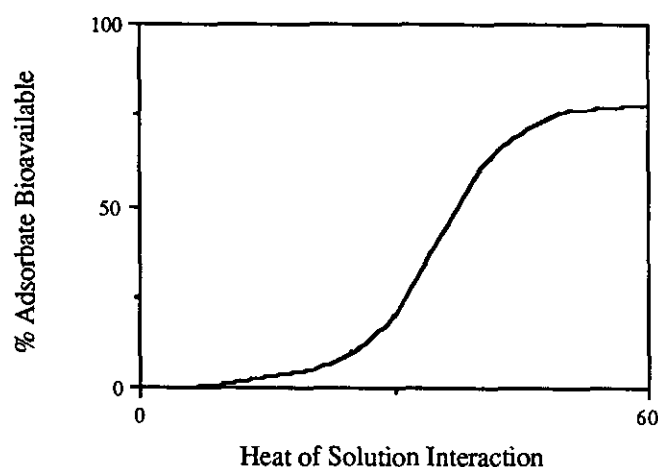


FIGURE 1. Bioavailability as a function of heat of solution interaction.

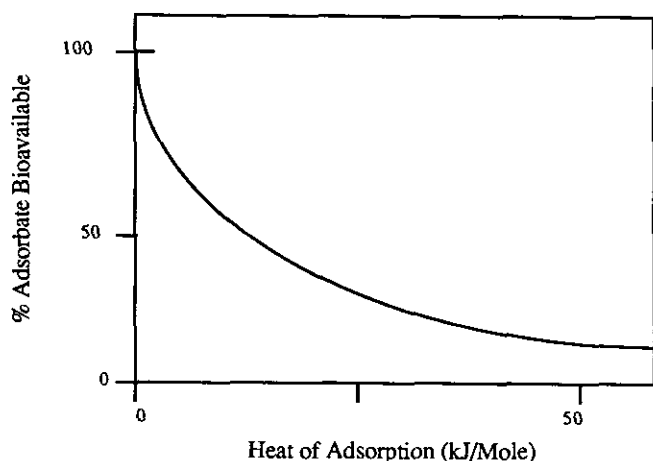


FIGURE 2. Bioavailability as a function of heat of adsorption.

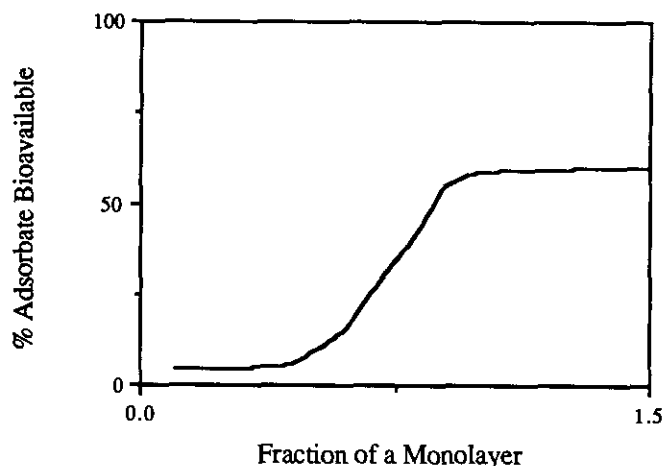


FIGURE 3. Bioavailability as a function of surface coverage.

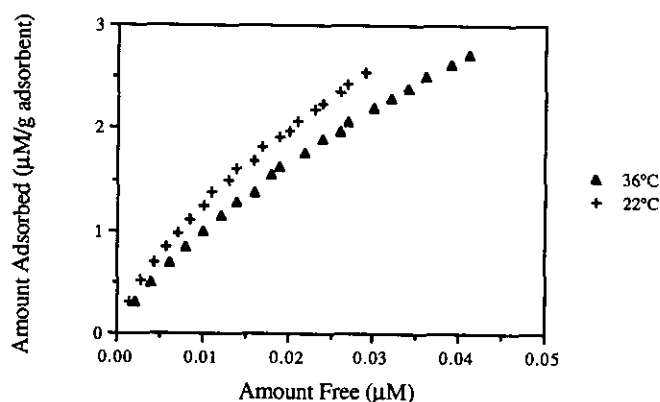


FIGURE 4. Adsorption isotherm for benzaldehyde on Black Pearls 2000 with dichloromethane as mobile phase.

fore would not be expected to displace solutes that interact more strongly. Most adsorbates are not expected to have high solubilities in water. Also, it should be mentioned that many of the solutes eluted by liquid-solid chromatography were not eluted at the column temperature investigated on the same carbon surfaces when adsorption was studied by gas-solid chromatography with pure solutes at low surface coverages.

Adsorption isotherms were also obtained from the solution elution peak shapes using a modification of the approach suggested by Saint-Yrieix (21). The computer programs developed to interpret gas-solid chromatographic data (1) were modified to generate solution isotherms and to obtain plots of the heat of adsorption as a function of surface coverage. Figure 4 shows the solution isotherms for the adsorption of benzaldehyde onto Black Pearls 2000 using dichloromethane as the mobile phase. These solution isotherms and values for the adsorption cross-sections of adsorbate molecules and the surface areas of the adsorbents (1) were used to obtain data for the heat of adsorption as a function of surface coverage (Fig. 5). There is reasonable agreement for the values of heats of adsorption obtained by the two

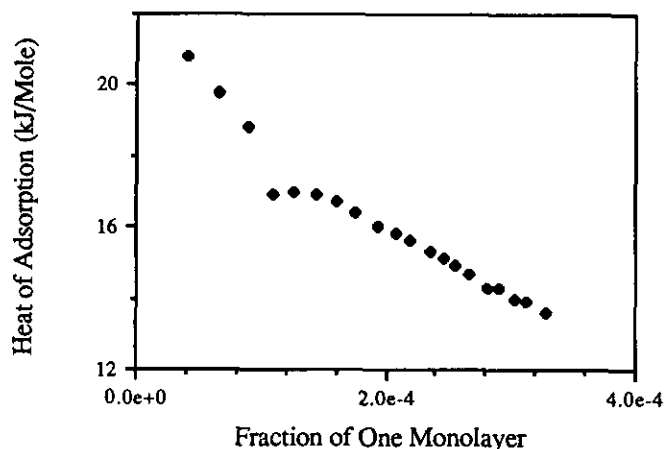


FIGURE 5. Heat of adsorption versus surface coverage for benzaldehyde on Black Pearls 2000 with dichloromethane as mobile phase.

approaches, providing that the shape of the eluting peak approaches Gaussian. This is consistent with the heat of adsorption obtained from shape of gas-solid chromatographic peaks reported previously by this laboratory (1). Only Gaussian gas-solid chromatographic peaks were obtained for adsorption on Black Pearls 2000, whereas Gaussian peaks were obtained for most adsorbents in liquid-solid chromatography, suggesting that the mobile phase reduced surface heterogeneities.

During the course of these studies, it became apparent that the use of standard elution liquid-solid chromatography may not be the optimum method to quantify the desorption of molecules from the surface of adsorbents that have been adsorbed in the gas phase (i.e., airborne particulate matter). The retention of a solute by column packing materials, in liquid-solid chromatography, is due to the relative affinity of the adsorbent surface for the mobile phase versus the solute molecules and is also due to the solubility of the solute in the mobile phase. Usually, if the solute is sparingly soluble in the mobile phase, then mixed mobile phases are used to increase solubility and hence improve peak shape. Also, there is still controversy on the actual mechanism responsible for retention in liquid-solid chromatography, since it has been proposed that retention could be due to the partition of the solute molecules into the thin film of adsorbed mobile phase. If this latter theory is correct, then modeling the desorption of gas phase adsorbed molecules by liquid-solid chromatography may be open to question because the solute could be interacting with adsorbed mobile phase rather than directly with the adsorbent surface. This latter theory is not consistent with the data previously discussed, as retention data would be independent of carbon.

A series of experiments were conducted in which selected solutes (benzene or benzofuran) were pre-adsorbed in the gas phase via a heated gas chromatographic inlet with the adsorbent column maintained at a temperature that did not elute the solute. These

preadsorbed solutes were then eluted by liquid solid chromatography using different mobile phases (1-hexane, methanol and water). The resulting data were interpreted in the same manner as usual liquid-solid chromatography. Since it is experimentally difficult to introduce solutes at concentrations comparable to liquid-solid chromatography (0.001  $\mu\text{L}$ ), solutes were introduced at concentrations that corresponded to fractions of the monolayer ( $\theta = 0.25$ ).

An added advantage of this method was that it used coverages that can be expected with environmental particulate complexes. The results of these studies were predictable based on the previous liquid-solid chromatographic data for the elution of the solutes using 1-hexane and methanol. The only differences observed were incomplete recovery of the solute from the columns and broader solute peaks. Peak broadening was due to gas phase preadsorption, which distributed the solute throughout the column, whereas liquid-solid chromatography introduces the solute as a plug. Also, the heats of desorption were slightly lower than the heats obtained by the usual elution method. The preadsorption method only quantifies the desorption of those molecules sorbed on the less active sites on the surfaces of the blacks, and the molecules adsorbed on high energy sites are retained. This conclusion was confirmed by the desorption data obtained for water, which desorbed benzene from the surfaces of N765, N339, and N339 ox, and benzofuran from the surface of N765. The elution profiles were broad, and significant irreversible adsorption was also apparent. It is interesting to note that even when coverages approached the monolayer, some solutes were irreversibly retained by selected adsorbents.

The conclusions that can be drawn from these two approaches are that normal elution liquid-solid chromatography can be used to quantify the release of low concentrations of molecules from the active sites on the surface of particles, and the preadsorption approach should be used for the release of molecules from particles that have coverages that correspond to a monolayer. The gas-phase preadsorption method has great environmental significance, as it supports the gas chromatographic data (1), which suggested that as surface coverage by adsorbed molecules increases and approaches the monolayer, the ease of release by physical processes can increase. The liquid chromatographic approaches were verified experimentally using static methods, and the resulting data were in agreement, although the static approach was experimentally more time-consuming and more open to error.

## Conclusions

There are a number of conclusions that may be drawn from this study that have a direct bearing on the interpretation of the risks associated with the inhalation of airborne particles of environmental origins. Adsorbed molecules can be released in differing amounts depending upon the polarity of the physiological fluid that in-



teracts with the surface. The significance of these findings is that a variety of solvents should be used to extract environmental particulate matter for *in vitro* biological assays, and solvents could be selected to remove compounds of interest by judicious choice in solvent polarity. Clearly, the carbon blacks proposed as models for environmental particles retain molecules selectively, and this selectivity is dependent upon the properties of the adsorbate, adsorbent, and of the releasing solvent. The extent of the release of molecules is also dependent upon the coverage and heterogeneity of the particle, and even though the particle may be subsequently coated with the physiological fluid, some strongly adsorbed molecules may not be available for rapid release. The interpretation of this conclusion using actual physiological fluids is currently receiving active investigation.

A controversial conclusion may be that the rapid release of adsorbed molecules results in transient acute effects, whereas the slow release produces long-term chronic effects. Also, since particles can still adsorb other exogenous molecules if their energies of interaction are greater than the energy of interaction of the molecules contained in physiological fluid with the particle surface, the particles could represent a sink for toxic molecules even after inhalation. These subsequently adsorbed molecules are expected to be released slowly to produce chronic effects. Soxhlett extraction of particulate complex may only remove those compounds that are released easily and does not release those compounds which produce chronic effects that may be more environmentally significant.

Although the mobile phases investigated in this study did not contain the zwitterionic character common to most biological tissues or fluids, they did have varying extended solvent parameters that are important contributors to the release of adsorbed molecules on the surface of inhalable particles. We are currently investigating the effects that polar active sites on the surfaces of particles may have on the selective capture and release of adsorbed molecules.

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